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TERNARY COMPOUND THIN FILM SOLAR CELLS

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The investigatic .f a group of ternary compound semiconductor (I-III-VI_2) thin films for future applications in photovoltaic devices is proposed. The consideration of these materials ($CuInSe_2$, $CuInTe_2$ and especially $CuInS_2$) for long-range device development is emphasized. The major objectives of this research include: (1) The identification and production of device-quality thin films of $CuInS_2$ on suitable substrates; (2) The demonstration of homojunction viability for $CuInS_2$ thin film solar cells; (3) The growth and characterization of $CuInSe_2$ and $CuInTe_2$ for photovoltaic application; and, (4) Possible heterojunction demonstration (e.g. p-type $CuInSe_2$ / n-type CdS thin film solar cell).

Much of the activity to date has been concerned with the growth and properties of $CuInX_2$ films. X-ray (Figs. 4-9) and electron diffraction analyses, Hall mobility and coefficient (Figs. 10, 13), resistivity and carrier concentration variations with substrate and film temperature (Fig. 11), as well as grain size data (Fig. 12) have been determined. Both p- and n-type films of $CuInS_2$ and $CuInSe_2$ have been produced. Single and double source deposition techniques have been utilized. Some data have been recorded for annealed films. (e.g. $CuInS_2$ in H_2S/Ar).

The physical and electrical characterizations of these films are to continue. Photoconductivity data and lifetime measurements are scheduled. A three-source deposition technique is being developed. Films are to be deposited onto several metal substrates, and a thorough investigation of contacts to the ternary films is underway. A tentative schedule (Fig. 15) accompanies this text.

The key results to date include:

(1) The deposition of $CuInS_2$, $CuInSe_2$ and $CuInTe_2$ films.

(2) Production of n- and p-type $CuInS_2$ and $CuInSe_2$ films on alumina substrates.

(3) Development of a double source deposition technique for $CuInS_2$.

(4) Report of electrical properties of $CuInS_2$ films.

(5) Report of x-ray and electron diffraction studies on ternary compound films.

FIGURE CAPTIONS

Fig. 1. Title Page

Fig. 2. Objectives

Fig. 3. Activity-To-Date

Fig. 4. Chalcopyrite Structure

Fig. 5. Calculated X-Ray Pattern: $CuInS_2$

Fig. 6. Calculated X-Ray Pattern: $CuInSe_2$

Fig. 7. Calculated X-Ray Pattern: $CuInTe_2$

Fig. 8. Tabulated X-Ray Data: $CuInS_2$

Fig. 9. Comparison of Single Phase and Multiple Phase Thin Films of $CuInS_2$ (X-Ray Diffraction Data)

Fig. 10. Mobility Dependence on Inverse Temperature. (a) Single Source Method, $T_{sub} = 280°C$; (b) Single Source Method, $T_{sub} = 160°C$; (c) Single Source Method, $T_{sub} = 400°C$. (d) - (i) Double Source Method. (d) $T_{sub} = 180°C$, $T_{sulphur} = 92°C$; (e) $T_{sub} = 220°C$, $T_{sulphur} = 92°C$; (f) $T_{sub} = 320°C$, $T_{sulphur} = 92°C$; (g) $T_{sub} = 400°C$, $T_{sulphur} = 92°C$; (h) $T_{sub} = 400°C$, $T_{sulphur} = 102°C$; (i) $T_{sub} = 400°C$, $T_{sulphur} = 108°C$. Film Thicknesses are 0.5μ; Substrates are Alumina.

Fig. 11. Resistivity and Carrier Concentration Dependence on Inverse Temperature. Curves (d') and (d") Correspond to Curve (d) on Fig. 10. ($T_{sub} = 180°C$). Curves (g') and (g") Correspond to Curve (g) on Fig. 10. ($T_{sub} = 180°C$).

Fig. 12. Grain Size Dependence on Substrate Temperature for Various Substrate Materials.

Fig. 13. Hall Coefficient as a Function of Substrate Temperature for Two Source Method. (a) $T_{sulphur} = 88°C$; (b) $T_{sulphur} = 92°C$; (c) $T_{sulphur} = 102°C$.

Fig. 14. Summary of Film Properties.

Fig. 15. Planned Activity.

TITLE PAGE

(a) TERNARY COMPOUND THIN FILM SOLAR CELLS

(b) University of Maine at Orono

(c) September 1, 1975 - August 31, 1976 (requested)

(d) $34,929. (requested)

(e) Lawrence L. Kazmerski
Associate Professor
Department of Electrical Engineering

Fig. 1.

OBJECTIVES

1. The Identification and Production of Device - Quality Thin Films of $CuInS_2$.

2. Demonstration of Homojunction Viability for $CuInS_2$ Thin Film Solar Cells.

3. Growth and Investigation of Other $CuInX_2$ Materials.

4. Possible Heterojunction Demonstration.

Fig. 2.

ACTIVITY-TO-DATE

1. $CuInS_2$

   (a) Development of Single and Double Source Deposition Techniques.

   (b) X-ray and Electron Diffraction Studies.

   (c) Initial Electrical Characterization of Films (μ, σ, n).

   (d) Production of n and p-type Films.

   (e) Recrystallization.

2. $CuInSe_2$, $CuInTe_2$

   (a) Film Deposition [illegible]rystallization.

   (b) Electrical Char[illegible]tion.

   (c) X-ray, Electron Diffr[illegible]ction Analyses.

Fig. 3.

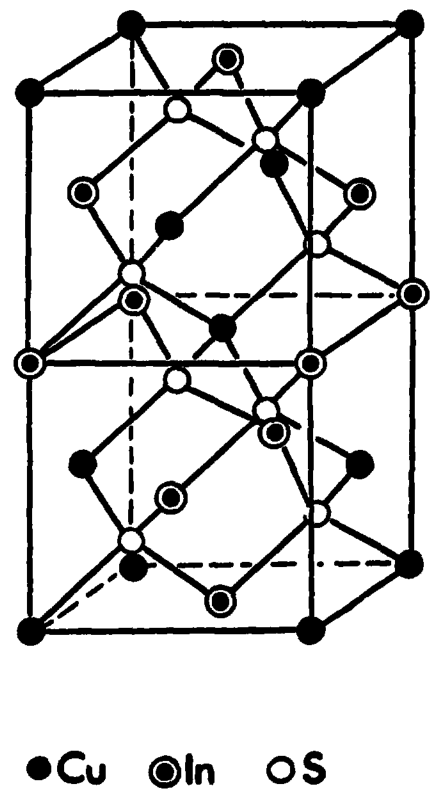


Fig. 4.

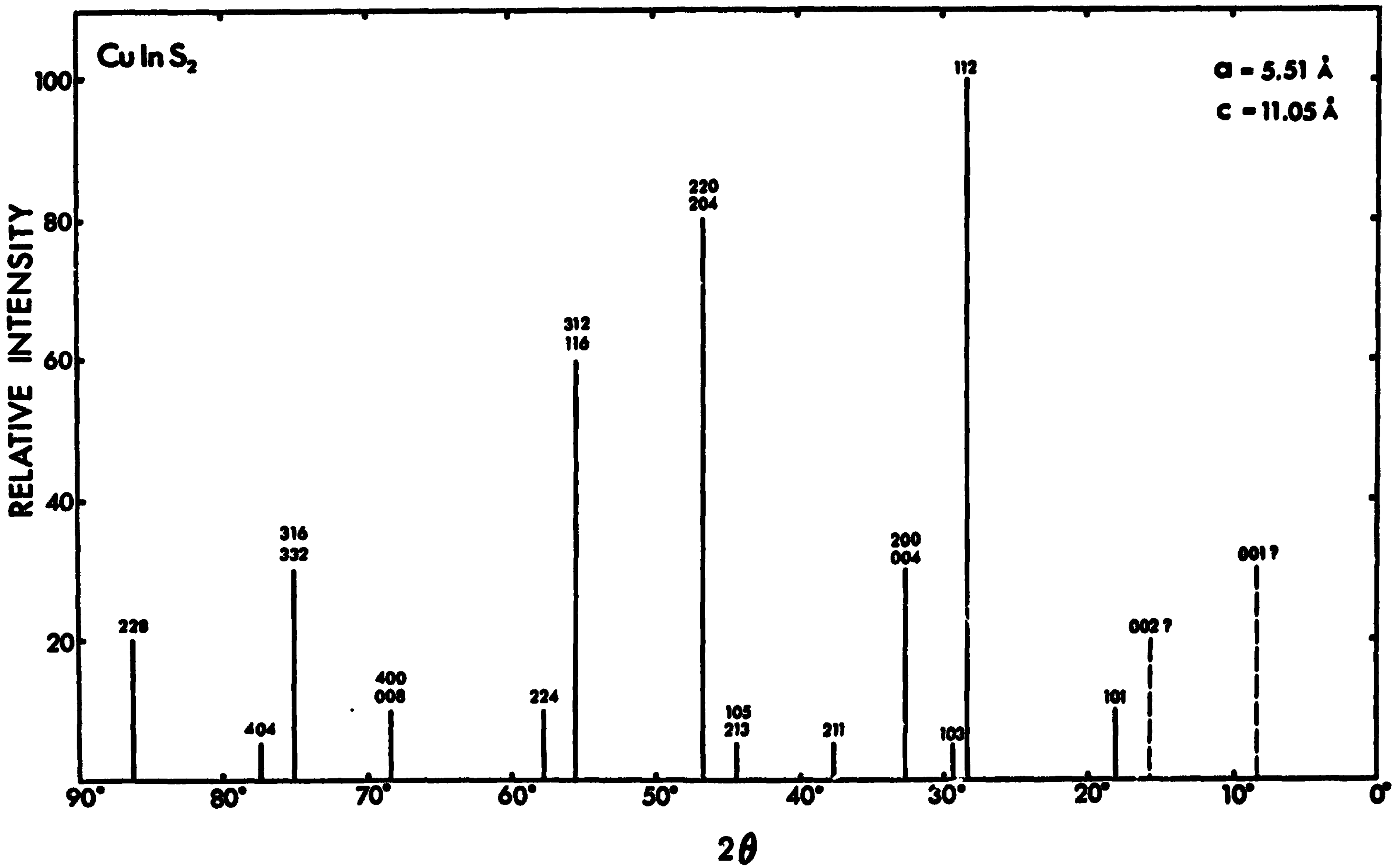
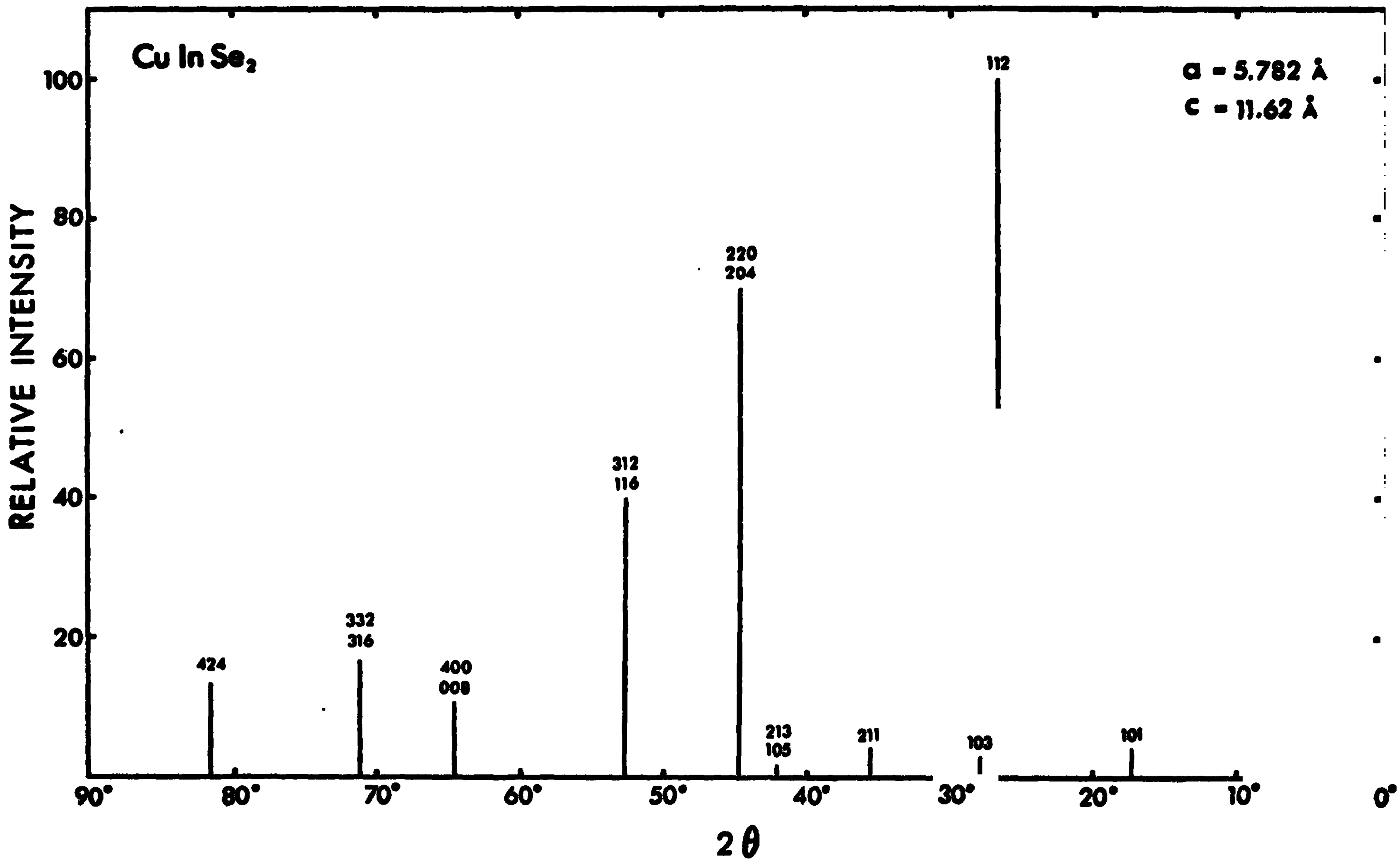

Cu In S_2
a = 5.51 Å
c = 11.05 Å
RELATIVE INTENSITY
100
80
60
40
20
112
220
204
312
116
316
332
200
004
001 ?
228
002 ?
400
008
224
105
213
101
404
211
103
90°
80°
70°
60°
50°
40°
30°
20°
10°
0°
2θ

Fig. 5.



Cu In Se2
a = 5.782 Å
c = 11.62 Å
RELATIVE INTENSITY
100
80
60
40
20
112
220
204
312
116
332
316
424
400
008
213
105
211
103
101
90°
80°
70°
60°
50°
40°
30°
20°
10°
0°
2θ

Fig. 6.

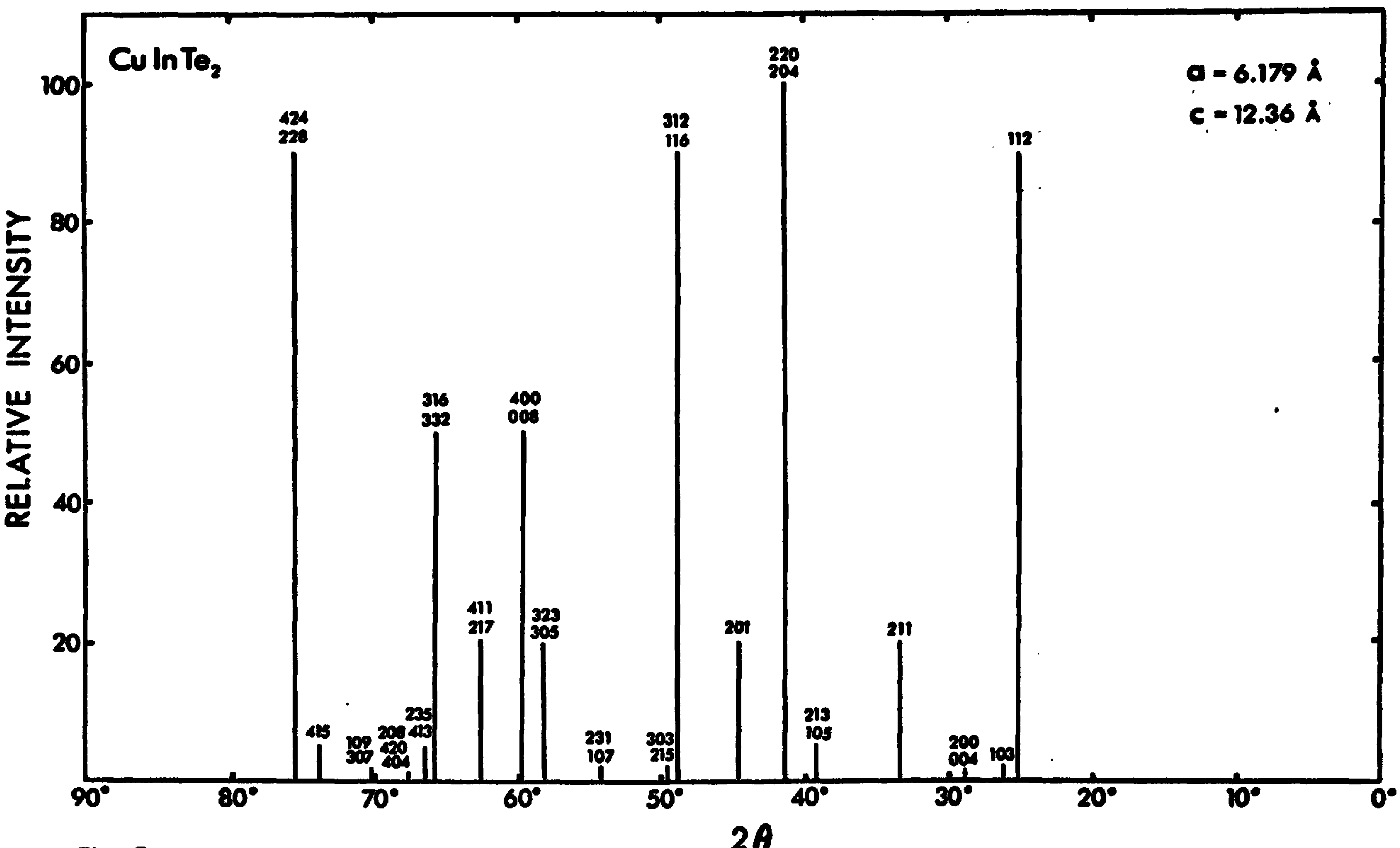

Cu In Te2
a = 6.179 Å
c = 12.36 Å
RELATIVE INTENSITY
100
80
60
40
20
90°
80°
70°
60°
50°
40°
30°
20°
10°
0°
2θ
424
228
415
109
307
208
420
404
235
413
316
332
411
217
400
008
323
305
231
107
303
215
312
116
201
220
204
213
105
211
200
004
103
112

Fig. 7.

TABLE II.

X-ray Diffraction Data (Calculated and Experimental Values)
For $CuInS_2$ Powders and Thin Films.
(Cu Kα and Cr Kα Radiation)

CALCULATED					OBSERVED 2θ		
d	2θ CuKα	2θ CrKα	hkl	Relative Intensity	Powder	Film CuKα	Film CrKα
10.6	8.34°		001?	30	--	--	--
5.56	15.94°		002?	20	--	--	--
4.87	18.20°	27.21°	101	10	18.16°	18.20°	27.2°
3.16	28.24°	42.51°	112	100	28.18°	28.18°	42.4°
3.04	29.38°	44.27°	103	5	29.28°	29.25°	44.2°
2.74	32.68°	49.42°	200,004	30	32.60°	32.60°	49.4°
2.39	37.64°	57.28°	211	5	37.52°	37.50°	57.2°
2.04	44.42°	68.32°	213,105	5	44.36°	44.22°	68.2°
1.94	46.84°	72.38°	220,204	80	46.66°	46.60°	72.3°
1.66	55.36°	87.27°	312,116	60	55.30°	55.28°	87.16°
1.591	57.98°	92.10°	224	10	57.88°	57.86°	92.1°
1.266	65.04	129.6°	316,332	30	64.92°	64.90°	--
1.128	86.24	--	228	20	--	--	--

Fig. 8.

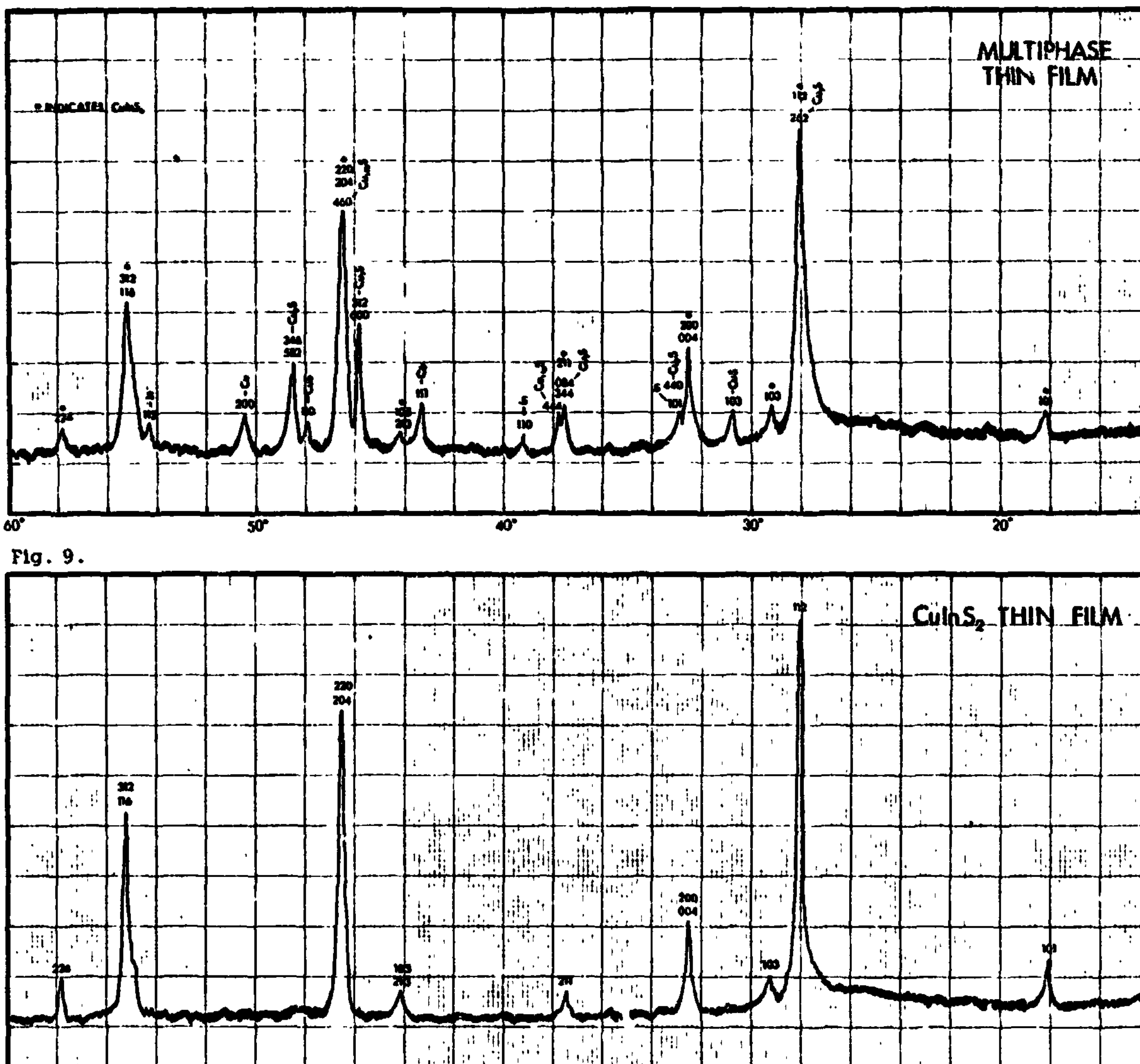
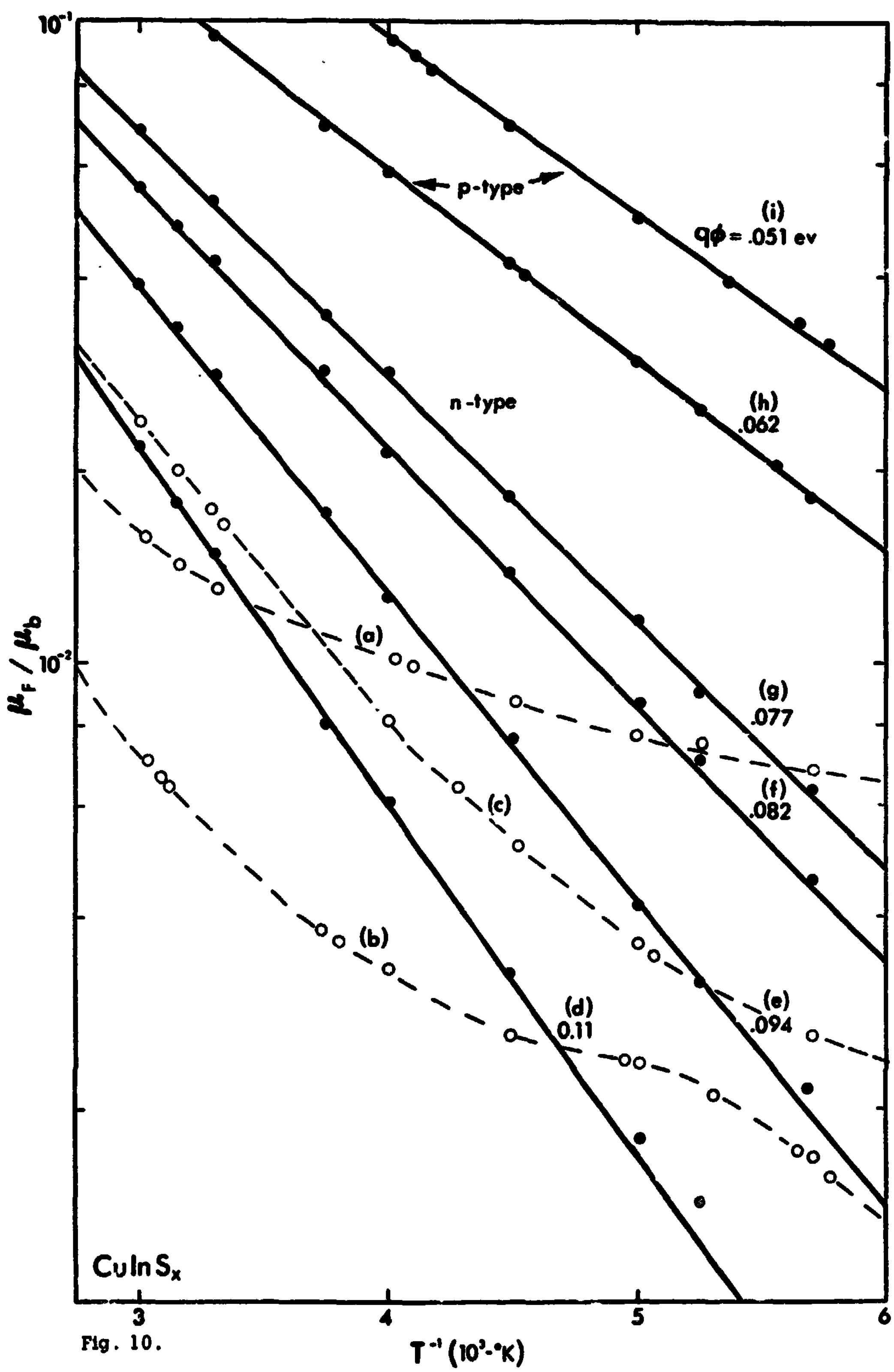


Fig. 9.



10^{-1}
10^{-2}
μ_F / μ_b
p-type
n-type
(i)
$q\phi$ = .051 ev
(h)
.062
(g)
.077
(f)
.082
(e)
.094
(d)
0.11
(a)
(b)
(c)
CuInS_x
3
4
5
6
T^{-1} (10^3-°K)

Fig. 10.

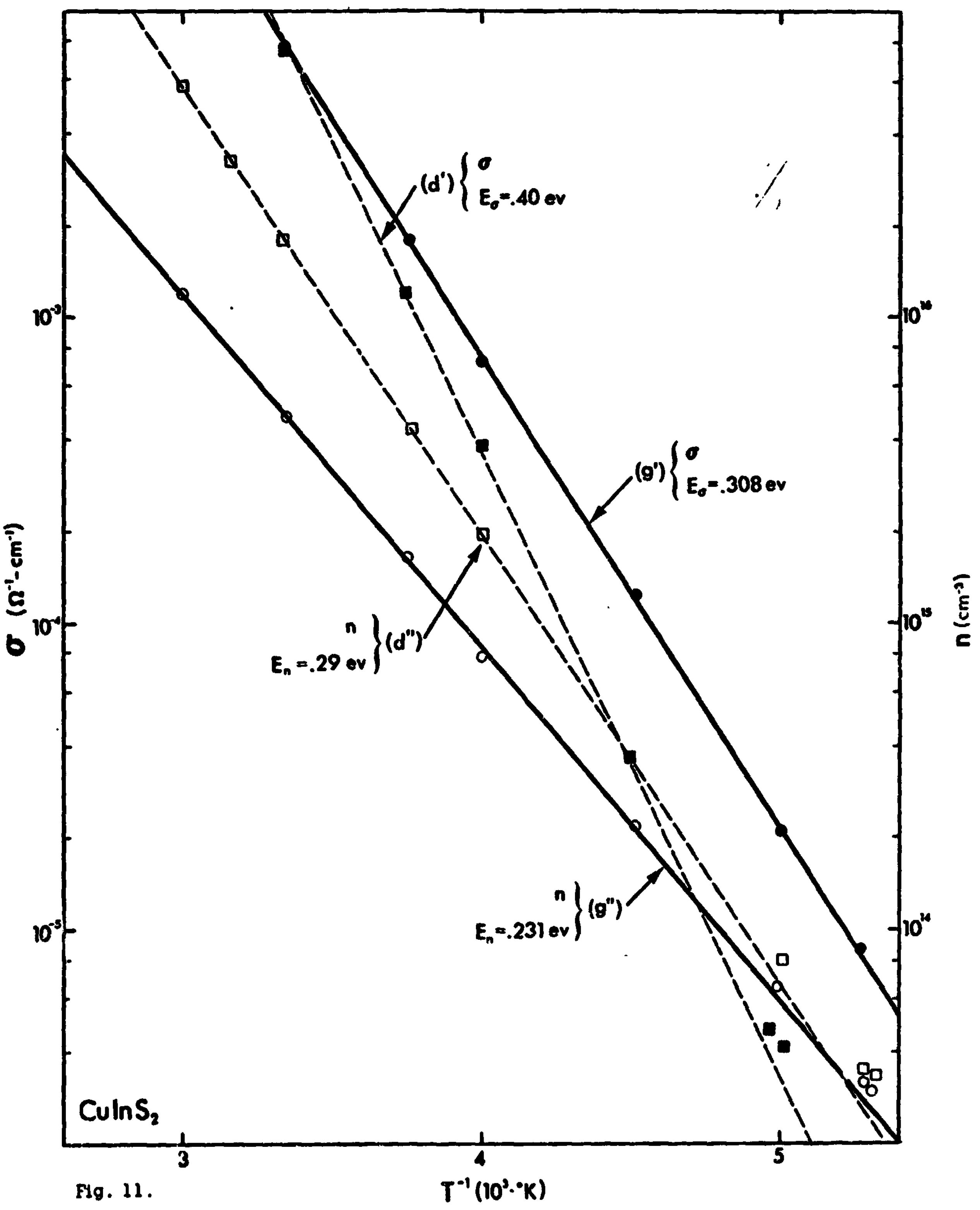
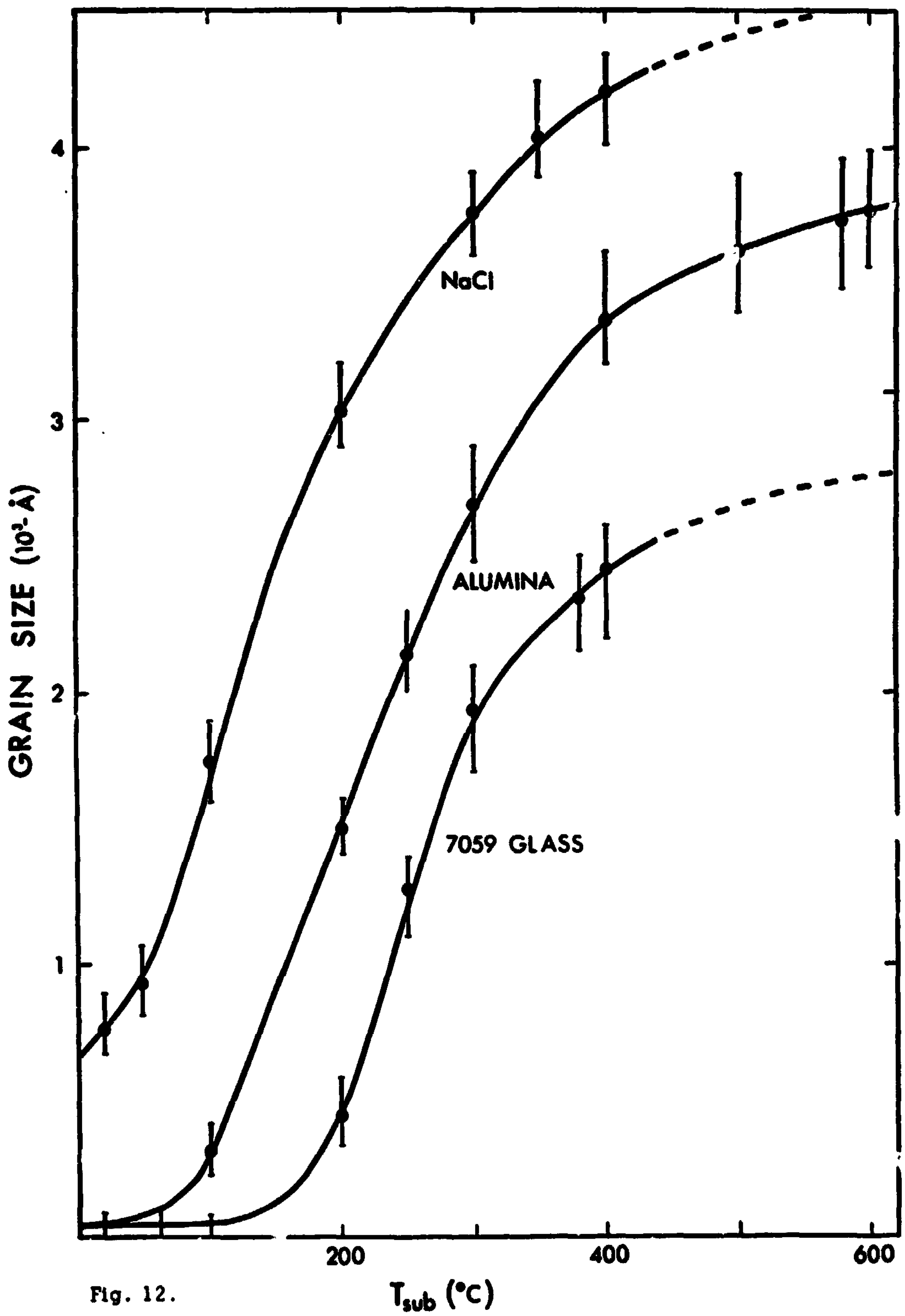

(d') σ E_σ=.40 ev
(g') σ E_σ=.308 ev
n E_n=.29 ev (d")
n E_n=.231 ev (g")
CuInS$_2$
σ (Ω^{-1}-cm^{-1})
n (cm^{-3})
10^{-3}
10^{-4}
10^{-5}
10^{16}
10^{15}
10^{14}
3
4
5
T^{-1} (10^3·°K)

Fig. 11.



NaCl
ALUMINA
7059 GLASS
GRAIN SIZE (10³ Å)
1
2
3
4
200
400
600
T_{sub} (°C)

Fig. 12.

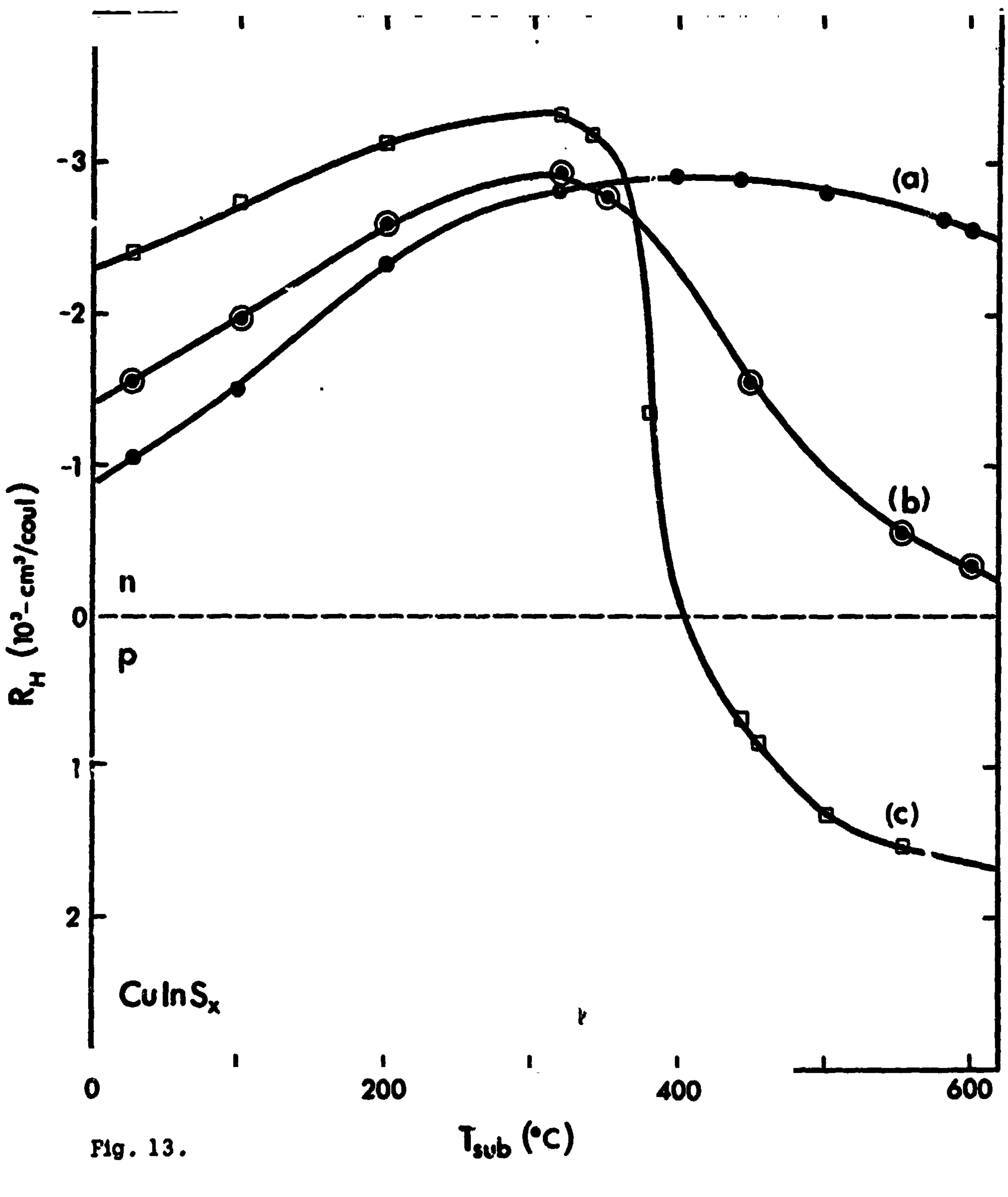


Fig. 13.

Table I. Comparison of properties of the deposited $CuInS_2$ thin films on this study with Single Crystal Values.

		Single Crystals[(a), (b)]				Films		
		ρ (Ω-cm)	n,p (cm^{-3})	μ ($\frac{cm^2}{v\text{-}sec}$)	E_g (eV)	ρ (Ω-cm)	n,p (cm^{-3})	μ $\frac{cm^2}{(v\text{-}sec)}$
$CuInS_x$	n	1	$3x10^{16}$	200	1.55	0.1-800	10^{14}-10^{19}	1-10;28[(c)]
	p	5	$1x10^{17}$	15		.8-400	10^{13}-10^{16}	~2;3.2[(c)];8.3[(d)]

(a) B.Tell, J.Shay and H. Kasper, Phys. Rev. B, 4, 2463 (1971)

(b) B.Tell and H. Kasper, Phys. Rev. B, 4, 4455 (1971).

(c) Recrystallized in H_2S, initially n-type.

(d) Recrystallized in H_2S, initially p-type.

Fig. 14.

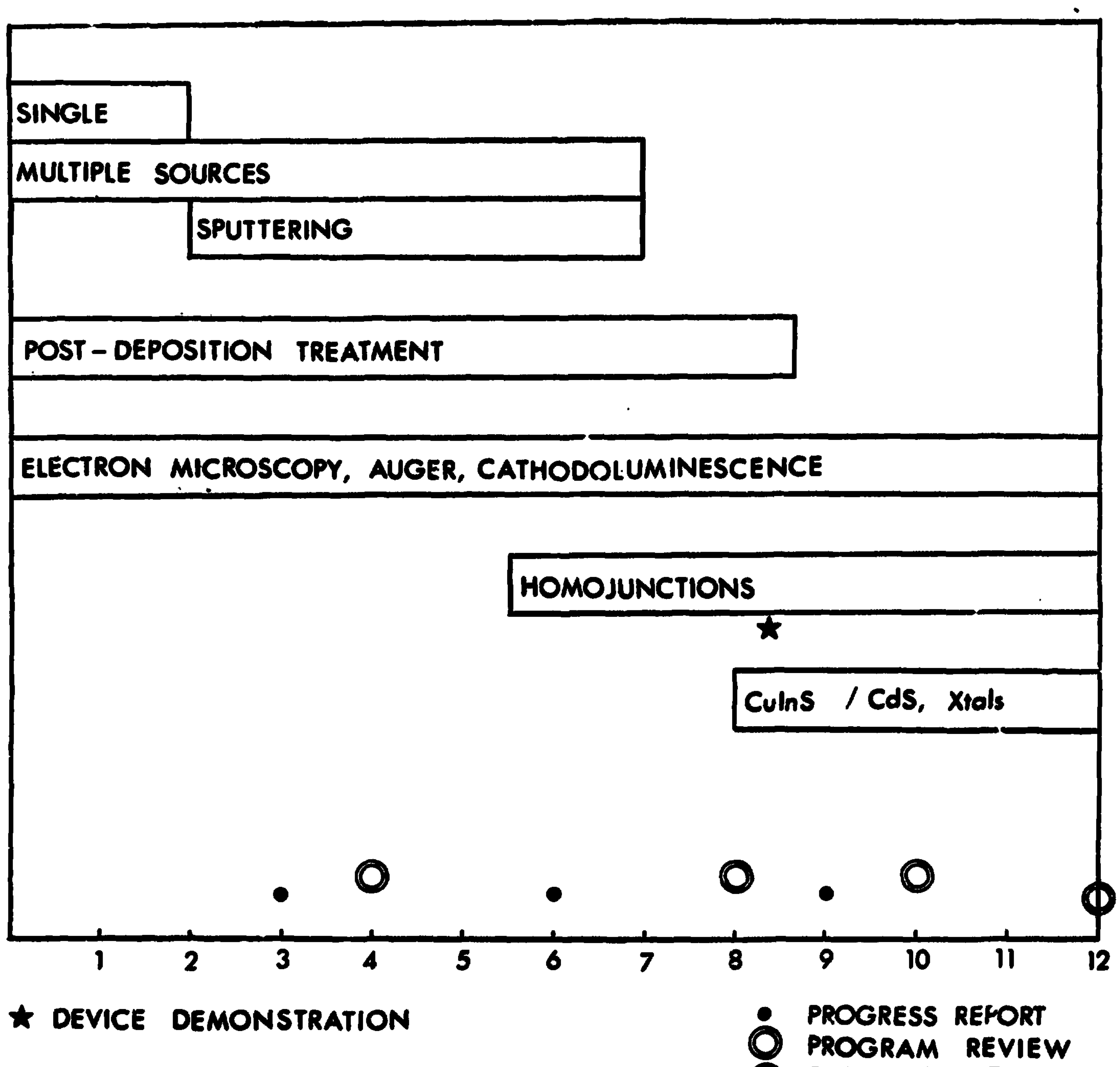

SINGLE
MULTIPLE SOURCES
SPUTTERING
POST – DEPOSITION TREATMENT
ELECTRON MICROSCOPY, AUGER, CATHODOLUMINESCENCE
HOMOJUNCTIONS
CuInS / CdS, Xtals
1 2 3 4 5 6 7 8 9 10 11 12
★ DEVICE DEMONSTRATION
PROGRESS REPORT
PROGRAM REVIEW
FINAL REPORT

Fig. 15.